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# Applied Catalysis B: Environmental

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## Photocatalytic carbon oxidation with nitric oxide

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### ARTICLE INFO

#### Article history:

Received 1 October 2014

Received in revised form

19 November 2014

Accepted 24 November 2014

Available online 3 December 2014

#### Keywords:

Titanium dioxide

Carbon

Nitrogen oxides

Photocatalytic removal

Simulated exhaust gas

### ABSTRACT

The photocatalytic oxidation of carbon black on TiO<sub>2</sub> using nitric oxide as an oxidizing agent was investigated. Layer-wise deposited carbon and TiO<sub>2</sub> powder was illuminated with UVA light in the presence of NO at parts per million concentrations in dry and hydrated carrier gas at a temperature of 150 °C. Carbon was photocatalytically converted mainly into CO<sub>2</sub>, and NO mainly into N<sub>2</sub>. Carbon oxidation rates of 7.2 μg/h/mgTiO<sub>2</sub> were achieved in the presence of 3000 ppm NO. Under these experimental conditions in the absence of molecular oxygen, formation of surface nitrates causing TiO<sub>2</sub> photocatalyst deactivation is suppressed. Addition of water enhances surface nitrate formation and catalyst deactivation.

NO and carbon particulate matter are air pollutants emitted by diesel engines. Elimination of soot collected on a diesel particulate filter through oxidation is a demanding reaction requiring temperatures in excess of 250 °C. The present study opens perspectives for a low-temperature regeneration strategy for the diesel particulate filter that simultaneously performs DeNO<sub>x</sub> reactions.

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### 1. Introduction

Particulate matter (PM) emissions generated in diesel engines have gained considerable attention due to the increasing number of diesel vehicles and due to their possible negative impacts on human health and environment [1–3]. There is increasing evidence on causal relationships between several diseases (e.g. cardiovascular and respiratory diseases) and chronic exposure to particulate matter [4,5]. The increasing concern has led to the introduction of more stringent exhaust emissions standards which necessitate the implementation of sophisticated exhaust gas purification systems in vehicles [6].

Currently, PM is removed from exhaust gas using a diesel particulate filter (DPF) [7]. PM trapped by DPF needs to be removed from the filter to avoid increasing backpressure which would degrade diesel engine performance. Periodic or continuous regeneration minimizes the risk of uncontrolled carbon burning in the filter [6]. Oxidation of retained PM to CO<sub>2</sub> in a diesel particulate filter is an evident way of filter regeneration. Oxidation of carbon using O<sub>2</sub> requires high temperatures of 500–550 °C [8]. Compared to O<sub>2</sub>, NO<sub>2</sub> is a much more powerful oxidizing agent. In continuously

regenerated PM traps, NO emitted by the engine is oxidized to NO<sub>2</sub> over an oxidation catalyst positioned in front [8]. NO<sub>2</sub> is able to oxidize carbon at temperatures as low as 250 °C [9–13]. Reaction mechanisms of the oxidation of carbon by NO<sub>2</sub> in the presence of water vapor and molecular oxygen are well documented [12–15]. In the carbon oxidation reaction, the NO<sub>2</sub> molecules are reduced mainly to NO:



Since the DPF does not eliminate NO<sub>x</sub>, an additional DeNO<sub>x</sub> system needs to be implemented to eliminate the NO downstream of the DPF [16,17]. Reduction of NO<sub>x</sub> using PM to N<sub>2</sub> instead of NO:



would eliminate the need of a separate DeNO<sub>x</sub> system downstream of the DPF.

Selective formation of N<sub>2</sub> has been observed in the reaction of carbon with NO in the temperature range 600–1000 °C [18]. The formation of CO<sub>2</sub> and CO can be described globally by Eq. (3) combined with Eqs. (4) and (5) [19,20]:



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The simultaneous elimination of two pollutants, viz. carbon particles and NO via reactions (3)–(5) is attractive in view of automotive applications, but the very high temperatures required for these reactions are impractical. The temperature of diesel exhaust gas in latest generation vehicles remains below the 250 °C threshold for regeneration, especially during urban driving conditions [21]. Regeneration of a DPF often necessitates additional heating, which is achieved by combustion of fuel injected in the exhaust gas, representing a fuel penalty.

Photocatalytic processes could be an attractive alternative for accelerating depollution reactions at low temperature. Titanium dioxide is a popular photocatalyst for air as well as water treatment [22,23], because of the large band gap energy of TiO<sub>2</sub> materials (anatase: 3.2 eV, rutile: 3.03 eV) these materials can only be activated by UVA light [24]. Application of TiO<sub>2</sub> on surfaces for pollutant removal through a solar-driven photocatalytic oxidation process in air is well documented [25,26]. Visual evidence of lateral and remote oxidation of soot by UVA-irradiated titanium dioxide thin films has been reported [27]. The elimination process of carbon particles on outdoor surfaces at ambient conditions is however quite slow [28]. Chin et al. developed a kinetic model of photocatalytic soot oxidation and assumed two pathways of CO<sub>2</sub> formation [29,30]: a direct soot oxidation to CO<sub>2</sub> and a multistep reaction for CO<sub>2</sub> generation from intermediate species of unknown nature. The oxidizing species generated by the photoactivation process are assumed to be superoxide anions (O<sub>2</sub><sup>•−</sup>) and hydroxyl radicals (HO<sup>•</sup>), derived from molecular oxygen and adsorbed water molecules, respectively [31–33]. Evidence from EPR and FTIR spectroscopy hinted at an essential role of molecular oxygen-related radicals in photocatalytic soot degradation [33]. Photocatalysis with TiO<sub>2</sub> has already been shown to be active in the reduction of NO<sub>x</sub> using ammonia (photocatalytic selective catalytic reduction or, in short, photo SCR), and in ammonia oxidation [34,35]. To our knowledge, no reports are available on the use of photocatalysis for performing the oxidation of carbon using nitric oxide as an oxidizing agent under conditions relevant to engine exhaust purification.

We investigated photocatalytic oxidation of carbon black in the presence of nitric oxide and water over commercial TiO<sub>2</sub> catalyst. We found that carbon can be photocatalytically oxidized into CO<sub>2</sub> under varied conditions. Furthermore, most of the NO is reduced to N<sub>2</sub>. Photocatalytic carbon oxidation with simultaneous NO<sub>x</sub> reduction is an attractive concept for future photocatalysis-assisted exhaust after treatment systems.

## 2. Experimental

### 2.1. Materials and sample preparation

Commercial TiO<sub>2</sub> photocatalyst (Cristal Global Millennium PC500) was used. This TiO<sub>2</sub> powder consists of anatase, has a surface area of 350 m<sup>2</sup>/g and a primary particle size of 9 nm [36]. Printex U is a popular model carbon black for evaluating carbon oxidation catalysis [37]. An amount of 5 mg of Printex U was deposited on a glass plate (300 mm × 50 mm) by spreading and evaporating an isopropanol suspension. Subsequently, 50 mg of TiO<sub>2</sub> catalyst powder was spread over the soot-coated glass plate using isopropanol solvent as described earlier [35].

### 2.2. Reactor set-up

The glass plate supporting the carbon and TiO<sub>2</sub> layer was placed in a flat photoreactor (Fig. 1).

The thermostatic support made of stainless steel is temperature-controlled and can be heated to 200 °C. The sample was illuminated

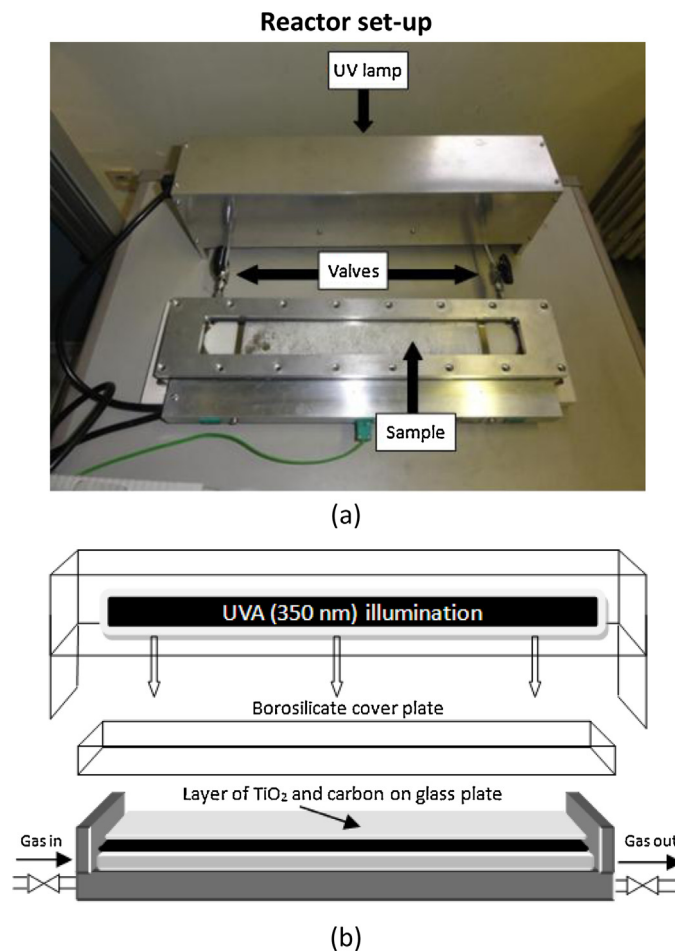


Fig. 1. Photograph (a) and schematic drawing (b) of the photoreactor.

from the top with a UVA-lamp (Rayonet) at a light intensity of 1.1 mW/cm<sup>2</sup>. The UVA lamp is mounted in an aluminum housing covering the reactor block. Sealing of the reactor is done by a borosilicate glass plate (430 mm × 70 mm) and Viton O-ring (Eriks). The headspace between the glass plate with deposited sample and the borosilicate sealing plate is ca. 2 mm high, creating a gas volume of ca. 48 cm<sup>3</sup>. NO (5% in He) and N<sub>2</sub> are fed from gas cylinders using mass flow controllers (Bronkhorst). Water vapor is introduced in the N<sub>2</sub> stream via a temperature-controlled bubbler. Analysis of the gaseous reaction products is conducted via a UV detector for NH<sub>3</sub>, NO and NO<sub>2</sub> (ABB Limas 11HW) and NDIR detector for N<sub>2</sub>O, CO and CO<sub>2</sub> (ABB Uras 26 instrument). The detectors have specific filters for each gas compound, minimizing interference with other gases. After passing through the UV detector, the gas is led through an ABB SCC-C gas cooler for removal of water in the gas stream and lowering of the dew point to 3 °C. All corrosive components (SO<sub>2</sub>, NH<sub>3</sub>, NO<sub>2</sub>) are transferred to the condensate for protection of the NDIR instrument. Both detectors are equipped with gas-filled cuvettes for autocalibration. The detection limits are less than 1% of the smallest measurement range (Table 1). The selectivity for N<sub>2</sub> was estimated from the nitrogen atom balance. Based on the detection limits, the standard deviation value was estimated at ±2% using the formula of cumulative uncertainty.

### 2.3. Carbon photocatalytic oxidation experiments

In a preliminary experiment, photocatalytic carbon oxidation was investigated under continuous flow of a gas mixture with 1000 ppm NO and 3% H<sub>2</sub>O in N<sub>2</sub> at a flow rate of 150 ml/min,

**Table 1**  
Measurement ranges and detection limits of gases.

Gas	Smallest measurement range (ppm)	Detection limit (ppm)
NO	0–100	<1
NO <sub>2</sub>	0–100	<1
SO <sub>2</sub>	0–50	<0.5
NH <sub>3</sub>	0–100	<1
N <sub>2</sub> O	0–100	<1
CO	0–400	<4
CO <sub>2</sub>	0–300	<3

corresponding to a volumetric hourly space velocity (VHSV) of  $187.5 \text{ h}^{-1}$  and a contact time of ca. 0.32 min. Under continuous flow, the concentration of CO<sub>2</sub> and CO in the outlet of the photoreactor was below the detection limit of the analyzers (ca. 1 ppm). The contact time was too short to enable detection of photocatalytic soot oxidation products. Therefore, the photoreactor was operated in batch mode as follows. First the reactor is purged under a flow of dry N<sub>2</sub> carrier gas at 150 °C for 30 min. Subsequently, reagent gas mixture is sent through the reactor in the absence of light. After 5 min, the gas inlet and outlet are closed and the carbon with photocatalyst sample is illuminated. At the end of an illumination period, the product gas mixture is conducted to the gas analyzers using N<sub>2</sub> carrier gas. Subsequently, the reactor is filled with fresh reagent gas, closed again and illuminated for another period.

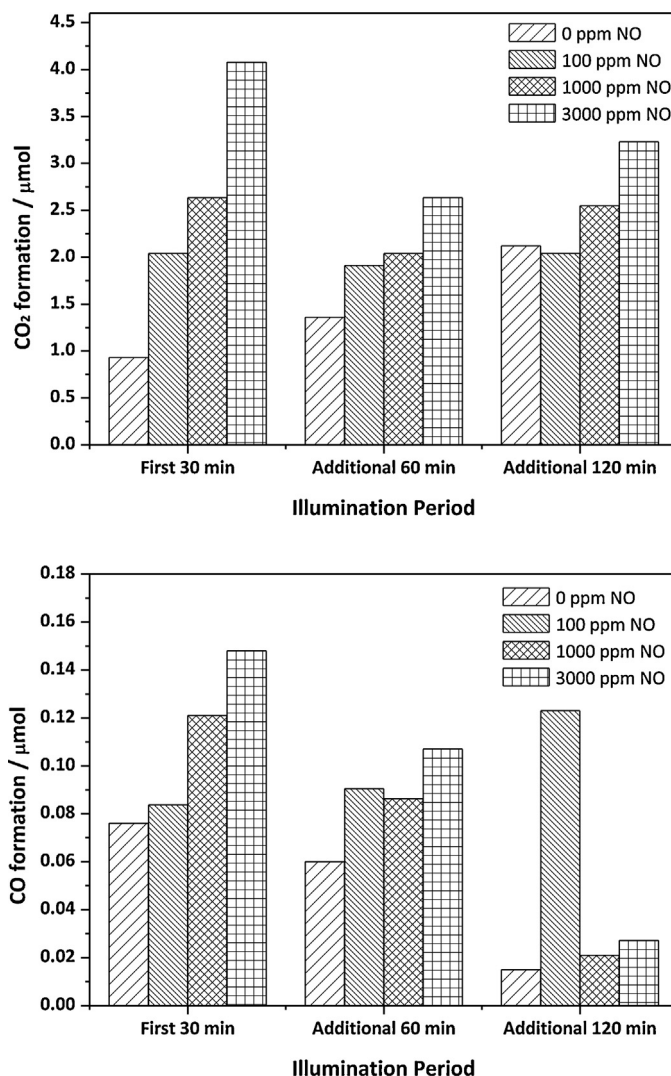
#### 2.4. FTIR spectroscopy

The formation of nitrates on the TiO<sub>2</sub> surface was investigated using Fourier Transform Infrared spectroscopy (Bruker IFS 66v/s FTIR instrument). The layer of TiO<sub>2</sub> after saturation with nitrate, and the layer of TiO<sub>2</sub> and carbon after photo-oxidation experiment were scraped from the glass support, diluted with KBr and pressed into a thin wafer. The TiO<sub>2</sub> content of the wafers was identical (0.5 mg in 473 mg KBr). The FTIR spectra were recorded under vacuum (residual pressure 3 mbar) at room temperature.

### 3. Results and discussion

UVA illumination of layer-wise deposited carbon black and TiO<sub>2</sub> powders was performed in the flat photoreactor presented in Fig. 1. Before starting the experiment, the reactor containing the carbon and TiO<sub>2</sub> was flushed at 150 °C with dry N<sub>2</sub> gas for preconditioning. Subsequently, reagent gas mixture is sent through the reactor in the absence of light for 5 min to get a steady flow of gas mixture. Then the reactor was filled with the selected gas mixture, closed and the UVA lamp switched on for 30 min. CO<sub>2</sub> and CO formation was quantified by flushing the reactor with N<sub>2</sub> and sending the gases to the analyzers. The procedure was repeated with 60 min illumination, and another time with 120 min illumination. Surprisingly, even under N<sub>2</sub> carrier gas without NO addition, CO<sub>2</sub> and CO were formed. During the first illumination, about 0.9 μmol CO<sub>2</sub> was formed (Fig. 2, Table 2). In the second illumination, CO<sub>2</sub> formation was enhanced and in the third illumination, CO<sub>2</sub> formation reached 2.1 μmol. Addition of NO to the gas phase enhanced CO<sub>2</sub> formation (Fig. 2, Table 2). The CO<sub>2</sub> formation in the first 30 min in the reactor filled with 100, 1000 and 3000 ppm NO amounted to 2.0, 2.6 and 4.1 μmol, respectively. Also in the second and third illumination period, the presence of NO enhanced CO<sub>2</sub> formation (Fig. 2, Table 2). The total quantity of CO<sub>2</sub> formed in the three illuminations in the presence of 100, 1000 and 3000 ppm NO amounted to 6.0, 7.2 and 9.9 μmol, respectively (Table 2).

CO was formed in much smaller quantities than CO<sub>2</sub> (Fig. 2, Table 2) in all reactions. In the first illumination period, there was a



**Fig. 2.** CO<sub>2</sub> and CO formation during three consecutive UVA illuminations of 5 mg carbon black on 50 mg TiO<sub>2</sub> in the presence of NO at different concentrations. T = 150 °C; N<sub>2</sub> carrier gas; no water vapor; 0–3000 ppm NO.

trend of enhanced CO formation with increasing NO concentration. In the second and third illumination periods, no obvious influence of NO on CO formation was observed. It is surprising that CO<sub>2</sub> and CO were formed when the reactor was filled with N<sub>2</sub> carrier gas only (Fig. 2, Table 2). In controlled experiments using soot without TiO<sub>2</sub> under illumination and in experiments in the dark with TiO<sub>2</sub> and carbon, there was no CO<sub>2</sub> nor CO formation, confirming the photocatalytic nature of the observed carbon oxidation. When the photoreactor is filled with N<sub>2</sub> carrier gas, the oxygen atoms of the CO<sub>x</sub> molecules must originate from the carbon black material itself or from TiO<sub>2</sub>, which under UV light in absence of oxygen can release some oxygen [38]. Carbon is known to be surface-oxidized and to have oxygen-containing organic groups on its surface. The carbon black sample of this study has an oxygen content of about 8 wt% [37,39]. Stoichiometric conversion of oxygen contained in the carbon to CO<sub>2</sub> can account for ca. 12.5 μmol CO<sub>2</sub> formation, which exceeds the actually observed quantity of 4.4 μmol under N<sub>2</sub> atmosphere after the three illuminations.

NO was reduced mainly to N<sub>2</sub> (Table 3), indicating that NO serves as an oxidizing agent. Filling the headspace of the reactor with NO at a concentration of 100 ppm corresponds to a supply of 0.23 μmol O-atoms. This quantity of O-atoms is insufficient to explain the CO<sub>2</sub> formation (2.0, 1.9 and 2.0 μmol in the three consecutive

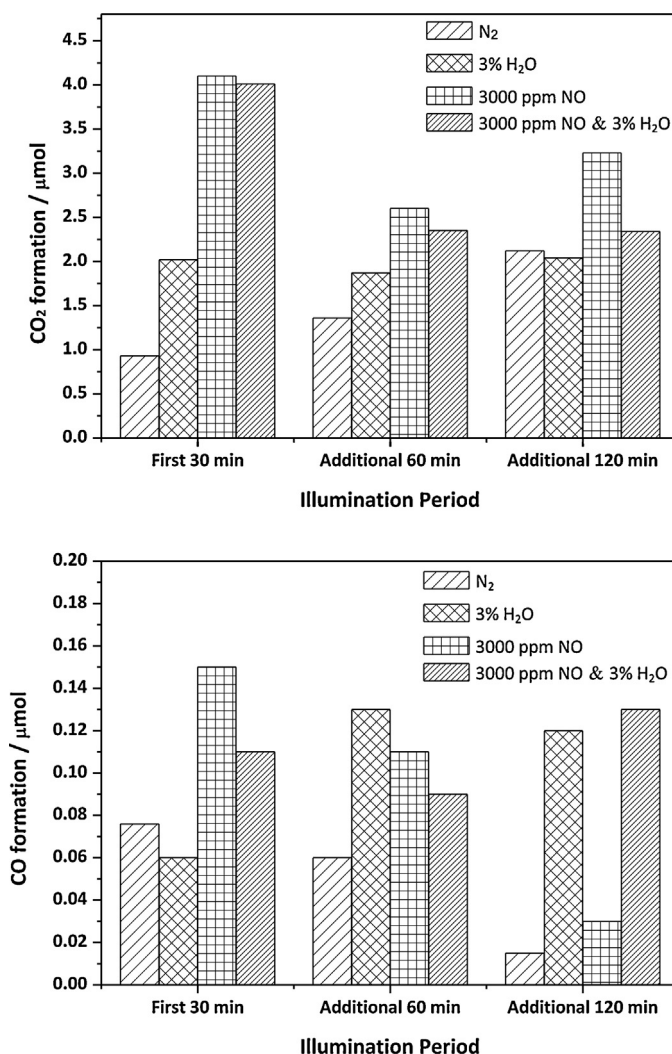


**Table 2**  
CO<sub>x</sub> formation under different reaction conditions.

Gas composition		Reaction time	CO <sub>x</sub> formation	
NO (ppm)	H <sub>2</sub> O (%)		CO <sub>2</sub> (μmol)	CO (μmol)
0	0	30 min	0.93	0.07
		Additional 60 min	1.36	0.06
		Additional 120 min	2.12	0.02
		Accumulative in 210 min	4.41	0.15
0	3	30 min	2.02	0.06
		Additional 60 min	1.87	0.13
		Additional 120 min	2.04	0.12
		Accumulative in 210 min	5.93	0.31
100	0	30 min	2.04	0.08
		Additional 60 min	1.91	0.09
		Additional 120 min	2.04	0.12
		Accumulative in 210 min	5.99	0.29
1000	0	30 min	2.63	0.12
		Additional 60 min	2.04	0.09
		Additional 120 min	2.55	0.02
		Accumulative in 210 min	7.22	0.23
3000	0	30 min	4.08	0.15
		Additional 60 min	2.63	0.11
		Additional 120 min	3.23	0.03
		Accumulative in 210 min	9.94	0.29
3000	3	30 min	4.01	0.11
		Additional 60 min	2.35	0.09
		Additional 120 min	2.34	0.13
		Accumulative in 210 min	8.7	0.33

illuminations, Table 2). Like in the experiment with carrier gas only, in this instance oxygen atoms originally contained in the carbon and the TiO<sub>2</sub> serve for CO<sub>x</sub> formation. Only at an NO concentration of 3000 ppm in the headspace of the reactor, the amount of O-atoms provided via NO matches the O-atom content of the CO<sub>x</sub> molecules formed.

In the absence of molecular oxygen, the reactive species generated by the TiO<sub>2</sub> photocatalyst likely are hydroxyl radicals (<sup>•</sup>OH), derived from water molecules [31–33]. This particular TiO<sub>2</sub> material after pretreatment at 150 °C contains ca. 3.7 wt% residual physisorbed water [35]. In a further series of experiments, the influence of intentional water addition to the gas phase was investigated (Fig. 3, Table 2). When N<sub>2</sub> carrier gas was loaded with 3% water vapor ca. 2.0 μmol CO<sub>2</sub> was formed in the first illumination (Fig. 3,



**Fig. 3.** CO<sub>2</sub> and CO formation during photocatalytic oxidation of 5 mg carbon black in the presence of 50 mg TiO<sub>2</sub> under four different atmospheres at 150 °C: N<sub>2</sub> carrier gas; 3% water vapor in N<sub>2</sub>; 3000 ppm NO in N<sub>2</sub>; 3000 ppm NO and 3% H<sub>2</sub>O in N<sub>2</sub>.

**Table 3**  
NO conversion and selectivity in photocatalytic carbon black oxidation.

Gas composition		Reaction time	NO conversion (%)	Selectivity (%)		
NO (ppm)	H <sub>2</sub> O (%)			N <sub>2</sub> O	NO <sub>2</sub>	N <sub>2</sub>
100	0	30 min	100	11	0	88
		Additional 60 min	99	7	0	93
		Additional 120 min	99	9	0	91
100	3	10 min	92	6	0	94
		Additional 10 min	93	2	0	98
		Additional 10 min	90	2	0	98
100	3	30 min	99	35	0	65
		Additional 60 min	92	1	0	99
		Additional 120 min	95	2	0	98
1000	0	30 min	98	19	0	81
		Additional 60 min	99	17	0	83
		Additional 120 min	98	12	0	88
3000	0	30 min	98	18	0	82
		Additional 60 min	98	13	0	87
		Additional 120 min	98	9	0	91
3000	3	30 min	66	26	0	74
		Additional 60 min	42	11	2	87
		Additional 120 min	45	8	3	89

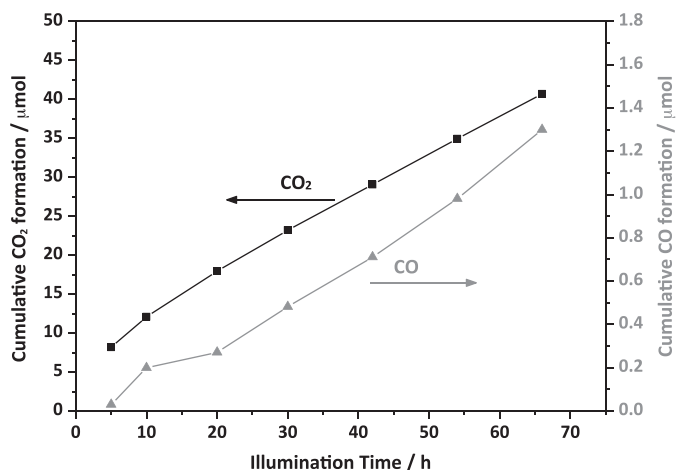


Fig. 4. Cumulative CO<sub>2</sub> and CO formation during long carbon photo-oxidation experiment in the presence of 3000 ppm NO and 3% H<sub>2</sub>O. Reaction temperature: 150 °C.

Table 2), which is more than the 0.9 μmol CO<sub>2</sub> formed using dry N<sub>2</sub> carrier gas (Fig. 2, Table 2), indicating an active role of water vapor. The favorable effect of water addition to the feed became less pronounced in the second and third illuminations. While in absence of NO water vapor had a positive influence on the carbon oxidation, addition of 3% water to a 3000 ppm NO containing feed had a slightly negative influence in each illumination period (Fig. 3, Table 2). The CO<sub>2</sub> formation over the three illumination periods amounted to 8.7 μmol in the presence of 3000 ppm NO and 3% water, compared to 9.9 μmol in the presence of 3000 ppm NO in dry gas (Fig. 3, Table 2). Water also suppressed NO conversion (Table 3). In the experiment with 3000 ppm NO and 3% water, the NO conversion was 66%, and decreased below 50% in the second and third illumination periods. In the experiment with 3000 ppm NO without water, after 30 min NO was almost completely converted (Table 3).

To verify the time needed for converting NO, an experiment with 100 ppm NO and 3% water was interrupted after 10 min of illumination (Table 3). The NO conversion amounted to 92%. The gas in the headspace of the reactor was refreshed and the illumination repeated. The NO conversion was similar to the first illumination (93%) and a third illumination with refreshed gas mixture yielded an NO conversion of 90%, with high selectivity (94–98%) for N<sub>2</sub>. Continuous illumination for 30 min, and subsequently for 60 and 120 min also resulted in almost complete conversion of 100 ppm NO (Table 3).

A long experiment was performed to verify whether substantial amounts of carbon can be photo-oxidized. Seven consecutive illuminations for 5 up to 12 h, each time with fresh gas mixture of 3000 ppm NO and 3% H<sub>2</sub>O in N<sub>2</sub> were applied. The oxidation progressed steadily (Fig. 4). In total, about 40.7 μmol CO<sub>2</sub> was formed together with 1.3 μmol CO, corresponding to an oxidation of about 10% of the carbon. The oxidation rate was ca. 2.9 μg carbon per hour and per mg TiO<sub>2</sub>. The highest carbon oxidation rate of ca. 7.2 μg carbon per hour and per mg TiO<sub>2</sub> was obtained in the experiment with 3000 ppm NO in dry gas, corresponding to ca. 2.3 nmol s<sup>-1</sup> (Fig. 2). Carbon oxidation through reaction with NO (Eqs. (4) and (5)) occurring at temperatures exceeding 600 °C [18] can be performed at 150 °C by applying TiO<sub>2</sub> photocatalyst. Light-duty vehicles produce on average 0.17 g km<sup>-1</sup> diesel soot [40]. Considering the average speed in the drive cycle of 34.1 km h<sup>-1</sup>, this corresponds to a PM production of ca. 5.8 g h<sup>-1</sup>. Photo-oxidation of this quantity of carbon would require about 0.8 kg of TiO<sub>2</sub>. This is of course a high amount, but it shows that optimization of the system and combination of thermal NO<sub>2</sub>-assisted carbon oxidation and photocatalysis could be an option. It can be expected that carbon photo-oxidation

Table 4

NO conversion and selectivity in long carbon photo-oxidation experiment (Fig. 4).

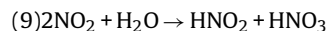
Illumination period/duration (h)	NO conversion (%)	Selectivity (%)		
		N <sub>2</sub> O	NO <sub>2</sub>	N <sub>2</sub>
1/5	98	15	0	85
2/5	81	11.7	0.3	88
3/10	98	9.9	0.1	89.9
4/10	91	10.9	0.7	88.4
5/12	91	12.1	0.7	87.2
6/12	87	13.0	0.9	86.2
7/12	83	13.7	1.0	85.3

will be further enhanced in the presence of molecular oxygen next to NO<sub>x</sub>.

The incident light intensity of this photoreactor is about  $2.9 \times 10^{17}$  photons s<sup>-1</sup>. Therefore, the formal quantum efficiency for this photocatalytic process is ca.  $4.8 \times 10^{-3}$  CO<sub>2</sub> molecules per photon. Assuming carbon oxidation to be a 4-electron redox reaction, an electron/photon formal quantum efficiency of 0.019 can be estimated from the formal quantum efficiency. This value is much higher than that reported in photocatalytic oxidation of burning 'T-lite' soot on TiO<sub>2</sub> coating under UVA irradiation ( $4.4 \times 10^{-4}$ ) [28].

The NO conversion and selectivity in the seven illuminations of Fig. 4 are reported in Table 4. The catalyst was most active in the first 5 h of the reaction achieving 98% NO conversion with 85% selectivity for N<sub>2</sub>. Trace amounts of NO<sub>2</sub> were formed during the reaction and N<sub>2</sub>O is the main by-product. The NO conversion decreased slightly in subsequent photo-oxidation.

Formation of surface nitrates is a documented cause of deactivation of TiO<sub>2</sub> photocatalysts [41]. Even in the absence of molecular oxygen, reaction pathways leading to nitric acid exist (Eqs. (6)–(8)). Nitrogen monoxide reacts with •OH radicals to HNO<sub>2</sub>, followed by reaction with •OH leading to NO<sub>2</sub> formation. Depending on the surface hydration, NO<sub>2</sub> can be released to the gas phase, or further oxidation with •OH to HNO<sub>3</sub> occurs [42]. NO<sub>2</sub> is a source of HNO<sub>3</sub>. NO<sub>2</sub> and HNO<sub>3</sub> can give rise to surface nitrates on TiO<sub>2</sub>.



Analysis of the gaseous reaction products (Table 3) revealed that only traces of NO<sub>2</sub> were formed in all experiments. The highest NO<sub>2</sub> formation was observed in the experiment with 3000 ppm NO and 3% water, using 30 min illumination (Table 3). Longer illumination times under this atmosphere lead to higher NO conversion and lower NO<sub>2</sub> concentrations, suggesting NO<sub>2</sub> to be an intermediate product. NO<sub>2</sub> can be involved in carbon oxidation (Eq. (1)) and nitrate formation reactions (Eqs. (8) and (9)).

The formation of nitrate was investigated using FTIR spectroscopy. For reference, a TiO<sub>2</sub> (50 mg) layer without carbon was saturated with nitrate in the photoreactor by applying a continuous flow of 30 ml/min of a gas mixture with 3000 ppm NO, 5% O<sub>2</sub> and 3% H<sub>2</sub>O in N<sub>2</sub> at 150 °C under illumination for 3 h. The FTIR spectrum of the TiO<sub>2</sub> (Fig. 5) shows a sharp absorption band at 1386 cm<sup>-1</sup> assigned to nitrate formed on the surface of TiO<sub>2</sub> photocatalyst [43]. The small peak at 1634 cm<sup>-1</sup> and the broad band around 3410 cm<sup>-1</sup> are ascribed to the bending and stretching vibrations of physisorbed water [33,44]. The broad peak centered at 530 cm<sup>-1</sup> is ascribed to bending of Ti–O bonds [45].

The mixture of residual carbon and spent TiO<sub>2</sub> photocatalyst recovered after the long photo-oxidation experiment (66 h) in the presence of 3000 ppm NO and 3% water (Fig. 4) showed similar FTIR bands (Fig. 5). The additional band at 1260 cm<sup>-1</sup>

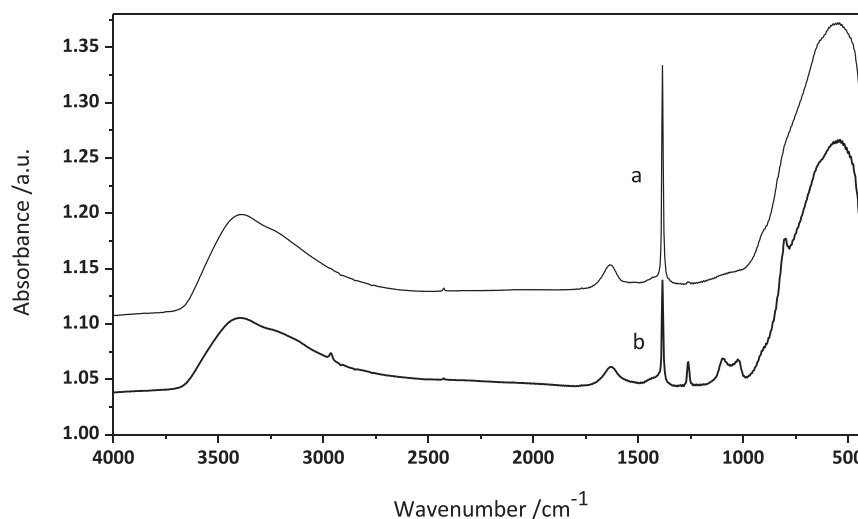


Fig. 5. FTIR spectra of nitrate-saturated TiO<sub>2</sub> photocatalyst layer (a) and of the mixture of TiO<sub>2</sub> and carbon black after 66 h photo-oxidation experiment of Fig. 4 (b).

in the carbon-containing sample may be caused by the C–O–C stretching in an anhydride and an aryl ether linkage in the carbon material [46,47]. The intensity of the nitrate band on the spent TiO<sub>2</sub> photocatalyst was lower than in the nitrate saturated reference. The maximum density of NO<sub>3</sub> groups on the TiO<sub>2</sub> surface has been reported to be around 0.5 molecules nm<sup>-2</sup> [41], corresponding to 1 NO<sub>3</sub>-group per 2 nm<sup>2</sup>. For the present TiO<sub>2</sub> sample with specific surface area of 350 m<sup>2</sup>/g, nitrate saturation would require 14.5 μmol nitrates. Assuming a same absorbance in the two samples, the nitrate content of the spent TiO<sub>2</sub> photocatalyst was estimated to be ca. 6.3 μmol nitrates. Compared to the ca. 62 μmol NO converted in the long experiment, the share of NO that is converted to nitrate is about 10%. In the calculation of the selectivity of NO conversion in Tables 3 and 4, nitrate formation was neglected, which, according to this FTIR study can be justified.

Nevertheless, the progressive coverage of the TiO<sub>2</sub> surface with nitrate may be responsible for the observed deactivation and the lower formation of CO<sub>2</sub> in subsequent illuminations in presence of NO (Figs. 2 and 3). The highest carbon photo-oxidation activity was observed in the presence of 3000 ppm NO in dry conditions (Fig. 3). The slight negative impact of water addition on carbon photo-oxidation (Fig. 3) may be explained by the nitrate formation according to Eqs. (6)–(8). At this stage of the research, we can only speculate on the reaction mechanism. Photocatalysis may provide a low-temperature reaction pathway to form NO<sub>2</sub>.

#### 4. Conclusions

The photocatalytic oxidation of carbon black layer deposited on TiO<sub>2</sub> coating at 150 °C is demonstrated. When a mixture of carbon and TiO<sub>2</sub> is illuminated in the absence of oxidizing agent, CO<sub>2</sub> molecules are formed from O-atoms originally contained in the carbon black and the TiO<sub>2</sub>. Nitric oxide is an effective oxidizing agent in the photocatalytic carbon decomposition. It is reduced mainly to N<sub>2</sub>, and to N<sub>2</sub>O. The highest carbon oxidation rate of 7.2 μg/h/mgTiO<sub>2</sub> was obtained using 3000 ppm NO in dry N<sub>2</sub> carrier gas. In the absence of water vapor, the residual water content of the TiO<sub>2</sub> and the carbon after pretreatment at 150 °C was sufficient for providing a source of reactive radicals. Addition of 3% water slightly decreased the carbon photo-oxidation activity. This observation can be explained by enhanced formation of surface nitrates poisoning the TiO<sub>2</sub> photocatalyst. Under the investigated reaction conditions, this deactivation by nitrate is a slow process. After 66 h of illumination about 40% of the TiO<sub>2</sub> surface is covered with nitrate.

Photocatalytic carbon oxidation at 150 °C is of potential interest in exhaust gas purification as photocatalysis could assist the regeneration of particulate filters at low temperature. An attractive feature is the reduction of NO to nitrogen, achieving DeNO<sub>x</sub> without the need of urea or other reducing agent. While NO<sub>2</sub>-driven regeneration necessitates a temperature of at least 250 °C, photocatalysis is taking place already at 150 °C. Photo-assisted carbon oxidation could be combined with the current thermally driven regeneration processes by implementing TiO<sub>2</sub> and UVA sources such as small LED lights in wall flow filter honeycombs. Currently, we are investigating the effect of molecular oxygen on the photocatalytic carbon oxidation process.

#### Acknowledgment

This work was supported by long-term structural funding by the Flemish government (Methusalem).

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## **Update**

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Volume 168–169, Issue , June 2015, Page 577

DOI: <https://doi.org/10.1016/j.apcatb.2015.02.002>





## Corrigendum

**Corrigendum to “Photocatalytic carbon oxidation with nitric oxide”  
[Appl. Catal. B: Environ. 166–167 (2015) 374–380]**

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The authors regret to inform that the numerical values of the carbon oxidation rates were incorrect.

In the long experiment of Fig. 4 the carbon oxidation rate was ca. 0.4  $\mu\text{g}$  carbon per hour and per mg  $\text{TiO}_2$ . The highest carbon oxidation rate of ca. 2  $\mu\text{g}$  carbon per hour and per mg  $\text{TiO}_2$  was obtained in the experiment with 3000 ppm NO in dry gas, corresponding to ca. 2.3  $\text{nmol s}^{-1}$  (Fig. 2). Photooxidation of carbon particles emitted by a light duty vehicle would require about 2.9 kg of  $\text{TiO}_2$ .

Authors would like to apologize for the inconvenience caused.

DOI of original article: <http://dx.doi.org/10.1016/j.apcatb.2014.11.051>.

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<http://dx.doi.org/10.1016/j.apcatb.2015.02.002>

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